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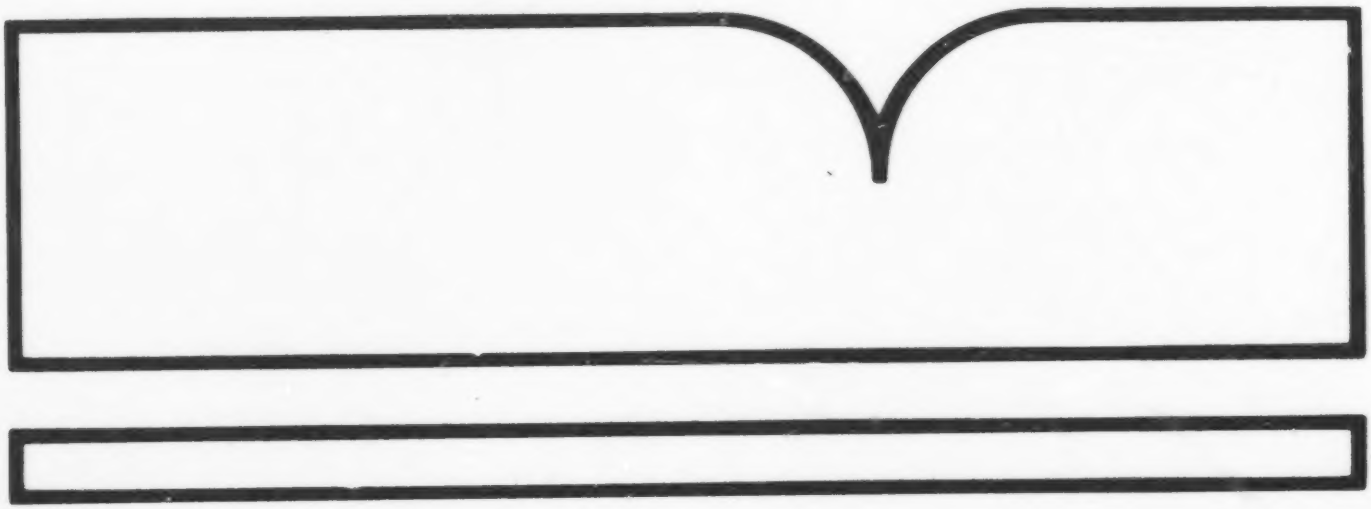
Recommended Operating Procedure No. 45
Analysis of Nitrous Oxide from Combustion Sources

Acurex Corp., Research Triangle Park, NC

Prepared for:

Environmental Protection Agency, Research Triangle Park, NC

Jun 90



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RECOMMENDED OPERATING PROCEDURE NO. 45: ANALYSIS OF NITROUS OXIDE FROM COMBUSTION SOURCES

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16. ABSTRACT The recommended operating procedure (ROP) has been prepared for use in research activities conducted by EPA's Air and Energy Engineering Research Laboratory (AEERL). The procedure applies to the measurement of nitrous oxide (N2O) in dry gas samples extracted from gas streams where N2O concentrations range from 0.5 to 200 ppm. N2O concentrations are interpreted by an electron capture detector (ECD). The ECD uses a 63Ni constant current cell. The upper limits of this procedure can be extended by changing the sample loop pressure to reduce the volume of sample in the look or by diluting the sample. ROPs describe non-routine or experimental research operations where some judgment in application may be warranted. ROPs may not be applicable to activities conducted by other research groups, and should not be used in place of standard operating procedures. Use of ROPs must be accompanied by an understanding of their purpose and scope.

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Disclaimer

This recommended operating procedure has been prepared for the sole use of the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

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SECTION 1

INTRODUCTION

1.1 SCOPE

This procedure is used to determine the concentration of nitrous oxide (N_2O) in gaseous post-combustion process streams. Any gaseous stream occurring after the combustion process may be considered a post-combustion process stream. Gas streams in ducts, fluidized beds, and stacks or flues are examples. Concentrations determined with this procedure are based on real-time (on-line) analysis or delayed analysis over time (grab sample).

This procedure is applicable to gas streams where N_2O concentrations range from 0.5 to 200 parts per million (ppm). The upper and lower limits can be extended by changing the sample loop volume; sensitivity limits are determined by the minimum detectable concentration of the standards.

1.2 LIMITATIONS

Recommended operating procedures (ROPs) describe non-routine or experimental research operations where some judgment in application may be warranted. ROPs may not be applicable to activities conducted by other research groups, and should not be used in place of standard operating procedures. Use of ROPs must be accompanied by an understanding of their purpose and scope. Questions should be directed to the preparers or project personnel listed in the Acknowledgments.

1.3 DEFINITIONS

- Accuracy - The degree of agreement between an average measurement ($\bar{X}$) and an accepted reference or true value (T) expressed as a percentage of the reference or true value; a data quality indicator. Accuracy includes a combination of random and systematic error or bias components which are due to sampling and analytical operations.

- Calibrate - To determine, by measurement or comparison with another standard, the correct value of each scale reading on a meter or other device. The levels of the calibration standards should bracket the range of planned measurements.

- Calibration Standard - A substance or reference material used to calibrate an instrument.

- Method Detection Limit (MDL) - The concentration corresponding to five times (5X) the background noise level of the measurement.

- Minimum Quantification Limit (MQL) - The concentration corresponding to 10 times (10X) the background noise level of the measurement, or the lowest calibration standard.

- Precision - The degree of variation among individual measurements of the same property, usually obtained under similar conditions; a data quality indicator. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms.

- Baseline Drift - The change in instrument output over a stated time period (usually 8 hours) of calibrated operation, when the initial input concentration is zero; usually expressed as a percentage of the full scale response.

SECTION 2

START-UP

2.1 APPARATUS

2.1.1 Equipment Needed

When equipment is first received, refer to the operation manuals for specific guidance in start-up and operating procedures for the gas chromatograph and the detector.

Gas Chromatograph (GC): Temperature- and time-programmable; capable of operating in a 50 to 200°C range; sample inlet equipped with dual mass flow controllers and a 10-port switching valve.

Precolumn: 1.8 m x 0.32 cm (6 ft x 0.125 in.) O.D. stainless steel, packed with 100/120 mesh support (e.g., Hayesep D by Alltech Associates, Inc., Deerfield, IL).

Analytical Column: 3.7 m x 0.32 cm (12 ft x 0.125 in.) O.D. stainless steel, packed with 80/100 mesh support (e.g., Porapak Super Q by Alltech Associates, Inc., Deerfield, IL).

Detector: Electron capture with ^{63}Ni constant current cell, capable of operating at 330°C.

Carrier Gas: Argon/methane mixture specifically prepared for electron capture detector (ECD) analysis; 90-95% Ar, 5-10% CH_4.

Data Acquisition System: Computerized peak measurement system tailored to gas chromatographic data.

Certified Calibration Gases: Four compressed gas cylinders of certified concentrations are required for calibrating the selected working range. Suggested working ranges are 0.5-5, 5-40, and 40-200 ppm. Nitrogen is the required balance gas for each cylinder.

Quality Control Standards: Three cylinders containing a known N_2O concentration which approximates the midpoint of each suggested working range.

Moisture Removal System: Refrigeration dryer or similar apparatus capable of condensing and removing moisture from sample stream. Desiccant trap containing P_2O_5 to remove remaining moisture.

Gastight Syringe: 5 cm^3.

2.1.2 Maintenance

Gas Chromatograph: Replace oxygen traps and molecular sieve at least every 6 months.

2.1.3 Theory of Gas Chromatography and Detection by Electron Capture

Gas chromatography (GC) refers to the separation technique where the constituents of a gaseous mixture (mobile phase) are transported through a heated column containing an adsorbing solid support (stationary phase). A GC system will generally consist of a pressurized cylinder of carrier gas equipped with a pressure regulator, sample injection system, analytical column, detector, and data recording system. A sample of unknown concentration is transported through the system by the carrier gas. To eliminate reaction with the sample or any component of the system, the carrier must be inert. The type of detection system used in the analysis will dictate the choice of carrier.

Separation is based on the attraction each constituent has for the stationary phase. A constituent's attraction for the stationary phase

determines the rate at which it passes through the column. Constituents having the least attraction will be adsorbed and eluted from the stationary phase more rapidly than those with a greater attraction.

As constituents elute from the analytical column, the detector produces an electrical signal proportional to the constituent concentration. The electron capture detector (ECD) uses two electrodes to produce this signal. One electrode is positively polarized and the other is treated with ^{63}Ni. The ^{63}Ni ionizes the carrier gas as it passes between the electrodes.

The ^{63}Ni emits high-energy electrons as it decays. These electrons produce large amounts of low-energy secondary electrons in the carrier gas which are collected by the other electrode. Sample constituents which have an attraction for secondary electrons cause a decrease in steady state current that is proportional to constituent concentration.

2.2 INTERFERENCES

Elimination or control of possible interferences to an analytical procedure is the responsibility of both sampling and analytical teams. Although the analyst must demonstrate on a daily basis that the analytical system is free from contaminants or residuals from previous analyses, certain precautions must also be observed by those persons responsible for obtaining the field sample. Known interferences to the measurement of N_2O in post-combustion gas streams include particulate matter, moisture, sulfur dioxide (SO_2), and halogenated organic compounds. Particulates must be removed during the initial sample extraction and before the gas enters the sample container (grab sample analysis) or the sample line (on-line analysis). An in-line filter may be used for particulate removal.

Moisture and SO_2 are two components of combustion flue gas which have been shown to influence N_2O generation in sample containers. Moisture is removed by pulling the sample through a non-reactive drying system such as

a refrigeration condenser or a desiccant trap containing a solid indicating agent. A refrigeration dryer and a column of P_2O_5 are the recommended drying systems. Use of these systems alone or in series will depend upon the percentage of moisture in the combustion gas.

CAUTION

Because of possible reaction with nitrogen oxides, silica gel should not be used as the indicating agent.

Interference from SO_2, residual moisture, and organics is controlled by a precolumn backflush system. The principal theory in this process is that, after the constituent of interest elutes from the precolumn, the effects of the remaining constituents are controlled by flushing the column with clean carrier gas. For example, the expected constituents in their respective order of elution include O_2, CO_2, N_2O, H_2O, SO_2, and some halogenated compounds. Since N_2O will come off the column before SO_2, backflushing the precolumn with carrier gas immediately following N_2O elution will protect the analytical system from the adverse effects of SO_2. The results of other studies have shown that halogenated compounds, such as fluorinated hydrocarbons and chlorinated hydrocarbons, will contaminate the ECD if they are not controlled. This contamination is usually seen as a long-term baseline upset. Again, the backflush system would eliminate organic interference because these compounds would typically come off the column after N_2O.

SECTION 3

OPERATION

3.1 SAMPLES/SAMPLING PROCEDURE

A sampling procedure which reduces the moisture and SO_2 levels in an extracted sample is under development. A detailed discussion of steps involved is beyond the scope of this procedure. The minimum sampling requirement for the analytical procedure is that the sample must pass through a moisture removal system before it reaches the analyzer or the sample container.

3.2 ANALYTICAL SYSTEM

The gas chromatograph (GC) must be capable of operating between 50 and 200°C. Since this procedure uses a precolumn backflush to minimize the effect of expected interferences, it may be considered a two-column procedure involving a 3.7 m x 0.32 cm (12 ft x 0.125 in.) O.D. stainless steel analytical column and a 1.8 m x 0.32 cm (6 ft x 0.125 in.) O.D. stainless steel precolumn. The columns must be preconditioned at 100°C-200°C before their initial use and subjected to an overnight conditioning at 75°C before each day's analysis. During analysis, the oven temperature should be 50°C.

The electron capture detector (ECD) with a ^{63}Ni constant current cell is operated at 300-350°C. Although the use of nickel as the energy source allows for operation at up to 400°C, it is recommended that the detector temperature be maintained in the indicated range since detector life is reduced at higher temperatures. The carrier gas, a mixture specially prepared for ECD analysis, contains argon and methane. The component ratio is 90-95% argon and 5-10% methane. The carrier gas initially flows through a 5 angstrom (Å) molecular sieve and an oxygen scrubber before it passes through the analytical system.

A schematic of the analytical system, including the precolumn backflush, is shown in Figure 1. A 10-port valve is used to direct the sample and the carrier gas, as one stream or as separate streams, through the analytical system. When the valve is in the "off" position, as seen in Figure 1(a), a sample coming into the 1 cm^3 fixed volume sample loop is circulated through the loop. At the same time, two streams of the carrier gas are circulated through the precolumn and the analytical column. The sample loop circulation is controlled by valve-ports 1, 2, 3, and 4. Flow for the precolumn backflush is controlled by ports 6, 8, 9, and 10. The gases exiting the sample loop and the precolumn are directed to vent. Ports 5 and 7 are used to direct the carrier flow to the analytical column. Gas exiting the analytical column is passed to the detector.

In the "on" position (Figure 1b), the bridges connecting the ports are realigned so that (1) the carrier gas stream flowing to the analytical column and the sample (from the sample loop) are combined to make up the mobile phase which passes through the precolumn, (2) the gas exiting the precolumn is directed to the analytical column and the detector, and (3) the second carrier gas stream (backflush) flows to vent. ECD response to calibration standards and samples is translated by a digital integrator.

The analysis of field samples will basically follow the steps outlined for instrument calibration in Section 4. The one exception is that, during analysis, the sample is initially injected onto the precolumn instead of the analytical column. After instrument calibration, the following steps are used to analyze grab samples:

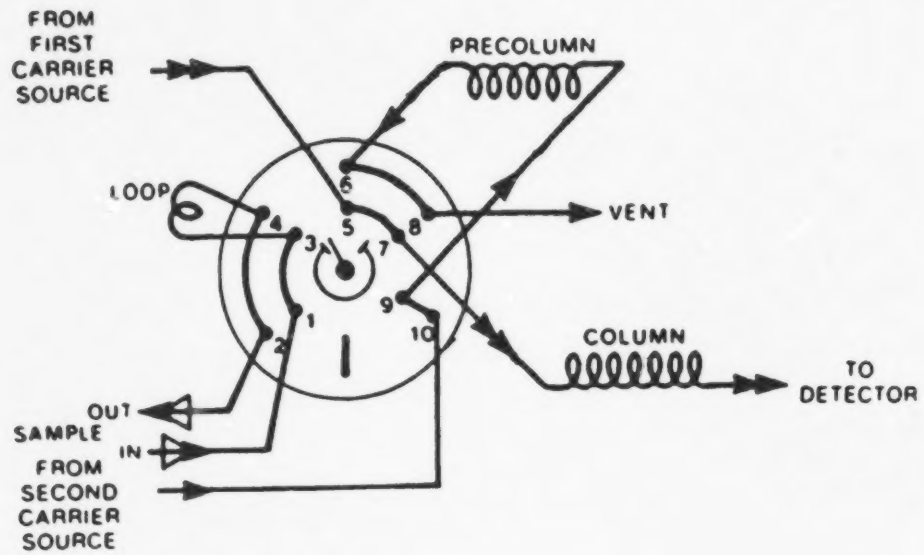
A. Adapt a septa fitting to the inlet of the sample loop.

B. Flush a 5 cm^3 syringe twice by filling the syringe with a sample of combustion gas.

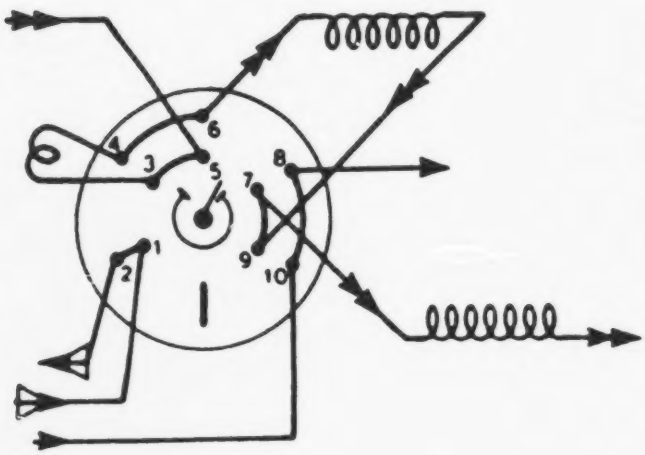
C. Inject a third 5 cm^3 sample into the sample loop.

D. At 0.1 minute, activate the 10-port valve so that the sample is loaded onto the precolumn. N_2O will elute to the analytical column in ~3.5 minutes.

E. At 3.5 minutes, turn the valve to the "off" position so that the precolumn is backflushed with carrier gas.



1a) Gas Sample with Backflush: Valve Off



1b) Gas Sample with Backflush to Vent: Valve On

Figure 1. Schematic of analytical system with precolumn backflush.

F. N_2O will elute from the analytical column at ~6.5 minutes. The total run time for analysis is ~8 minutes.

G. Introduce another 5 cm^3 sample into the sample loop. Repeat steps C-F until three data points (peak areas) are obtained for the sample.

H. Calculate the average peak area. Calculate the N_2O concentration according to equation (4) in section 4.2.

For on-line analysis, a stainless steel tee is used to connect the GC inlet to the main sample line from the combustion source. The sample flows from the source, through the sample conditioning system (moisture removal), and then directly to the GC inlet. Using this method of direct injection, instead of syringe injection, on-line analysis is accomplished by following the preceding steps D-H for analysis of grab samples.

3.3 GC OPERATION

3.3.1 Standards

A. Four compressed gas cylinders of certified concentrations are required for calibrating the selected working range. Suggested working ranges are 0.5-5, 5-40, and 40-200 ppm. Nitrogen is the required balance gas for each cylinder. Outfit each cylinder with appropriate pressure regulators. These gases will be used to conduct the multipoint calibration.

B. Three commercially prepared compressed gas cylinders certified to contain N_2O concentrations approximately equal to the midpoint of each suggested working range are required. These gases will be used to conduct quality control (QC) checks during analysis.

C. Verify the stability of the certified concentration of each cylinder of gas.

3.3.2 Precalibration

A. With the GC power off, open the main valve of the carrier gas cylinder and set the pressure to 482.36 kPa (70 psig).

B. Adjust the carrier gas flow to approximately 30 cm^3/min.

C. Turn the power on.

D. Set the oven temperature to 75°C, and allow the temperature to stabilize.

E. Condition the analytical column and the precolumn overnight at 75°C. Both columns should be conditioned overnight prior to each day's analysis.

SECTION 4

TROUBLESHOOTING

4.1 MULTIPOINT CALIBRATION

The multipoint calibration must be performed for initial start-ups if the analytical system is subjected to a full shutdown, or if the carrier gas cylinder is changed. The calibration must complement the type of sample to be analyzed. If grab samples are analyzed, the calibration must be by syringe injection. For on-line analysis, calibration must be accomplished through direct injection from compressed gas cylinders.

Calibration data points are generated with standards of known concentration. The calibration concentrations must bracket the expected sample concentrations. The following procedures must be conducted prior to analysis of samples.

CAUTION

Do not connect pressurized gas cylinders directly to the gas chromatograph. Use a sample valve to avoid damaging the instrument.

4.1.1 Calibration for Grab Sample Analysis

A. Remove the end cap from the ECD inlet and connect the detector to the GC.

B. Set the detector temperature to approximately 20°C below the maximum operating temperature (e.g., 330°C if maximum temperature is 350°C).

C. Allow the analytical column and the precolumn to cool to 50°C.

D. Access the data acquisition system.

E. Verify the stability of the column temperatures.

F. Connect a septa to the outlet of the sample line that is attached to the pressure regulator of the gas cylinder containing the lowest concentration calibration standard, or transfer a portion of the standard to a clean sample container (bomb) equipped with a septa. To transfer the standard:

1. Purge a bomb with the lowest concentration of standard for sufficient time to allow at least 10 liters of gas to flow through the container.

2. Close the valve on the bomb inlet, turn off the cylinder at the regulator outlet, and allow the sample container to equilibrate to ambient pressure.

3. Close the valve on the bomb outlet.

4. Repeat steps 1-3 with the remaining standards.

G. Using a 5 cm^3 gastight syringe, extract a sample of the lowest concentration calibration standard. Introduce the sample into the GC inlet. Repeat the injection to ensure that dead space in the syringe tip does not dilute the sample. Allow the sample to reach equilibrium in the sample loop.

H. Inject the sample into the sample loop. Set the GC to run, and load the sample onto the analytical column.

I. After approximately 3.5 minutes, return the GC to the load (backflush) position.

J. N_2O will elute from the column in approximately 6.5 minutes. Measure the ECD response (as integrated peak area) to the calibration standard.

K. Repeat steps G through J until three data points are obtained.

L. Calculate the average integrated peak area (PA).

M. Repeat steps G through L for the remaining standards.

N. To derive the calibration curve, follow steps A-D outlined in section 4.2.

4.1.2 Calibration for On-Line Analysis

A. Follow steps A through E in the procedure for grab sample analysis (section 4.1.1).

B. Adjust the regulator for the cylinder containing the lowest concentration of N_2O to 34.47 kPa (5 psig).

C. Using a Teflon sample line, connect the cylinder to the GC at the sample loop inlet.

D. Open the regulator valve and allow the sample loop to fill. Close the valve, and allow the sample to reach equilibrium. Load the sample onto the analytical column.

E. Measure the ECD response (as integrated peak area) to the calibration standard. Repeat the measurement and obtain three data points.

F. Calculate the average integrated peak area (PA).

G. Repeat steps B through F for the remaining standards.

H. To derive the calibration curve, follow steps A-D in section 4.2.

4.2 LINEARITY CHECK

Figure 2 shows that the ECD output is a non-linear function of concentration. The relationship between the two variables, concentration and average peak area, exhibits a bow at the lower end of the curve. Figure 3 shows an expanded view of the lower end of the curve. To minimize and control relative error, it is recommended that a log transformation be performed on the original variables. Refer to section 5.1 for a detailed discussion of transformed curves. The transformed data are used to derive a least-squares linear regression. The equation for the curve would be of the form:

$$\ln(y) = \ln(a) + b[\ln(x)] \qquad (1)$$

where: $\ln(a)$ = the intercept of the calibration curve, and
b = the slope of the calibration curve.

A. Calculate a linear regression curve using the logarithm of each data point with y = ln (average peak area) and x = ln (concentration).

B. Verify the acceptability of each calibration curve by back-calculating the concentration of each calibration standard. Apply the log of the average peak area (y) to the regression, where:

$$\ln(x) = \frac{\ln(y) - \ln(a)}{b} \qquad (2)$$

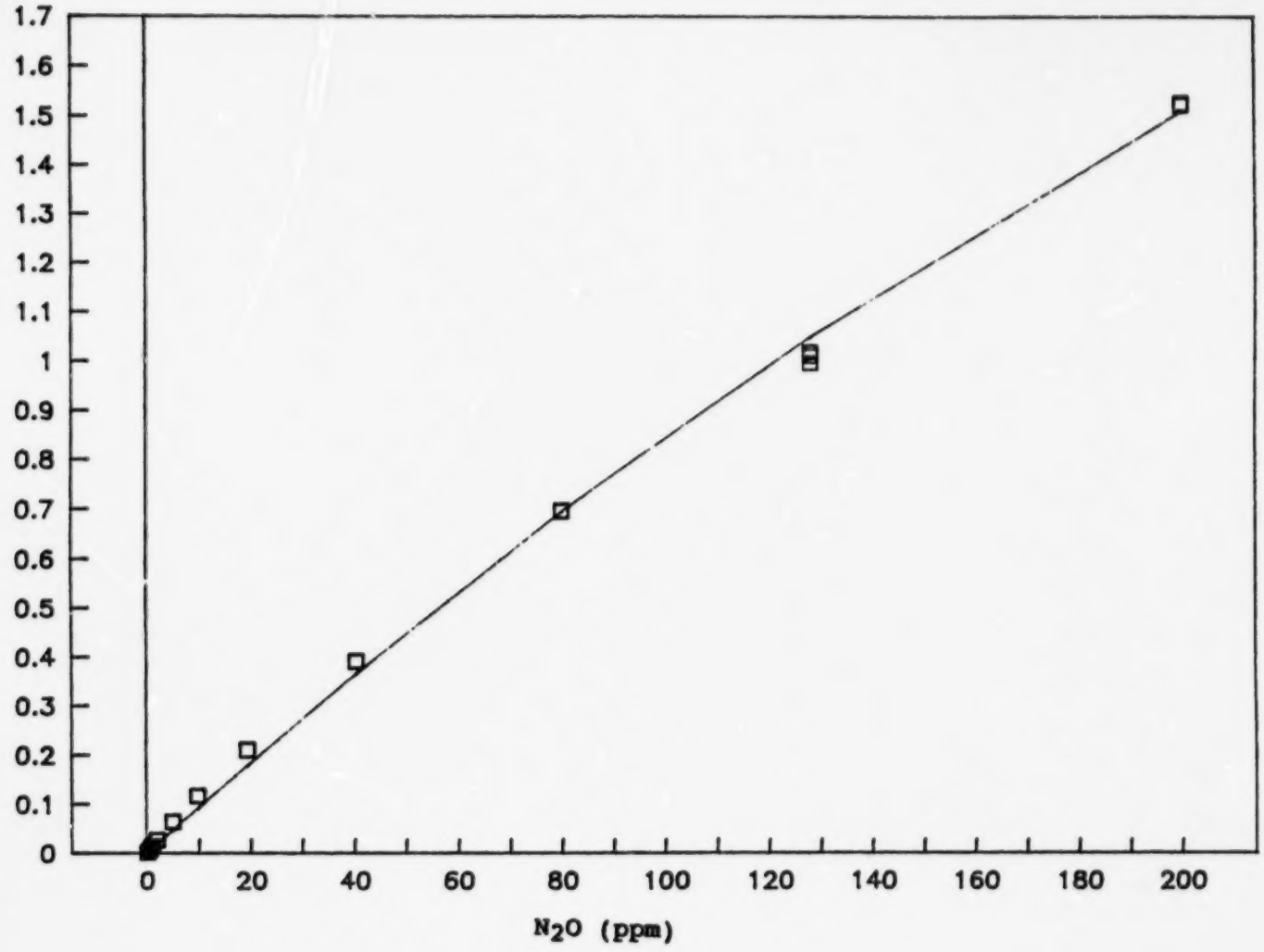


Figure 2. ECD response: 0.5-200 ppm range.

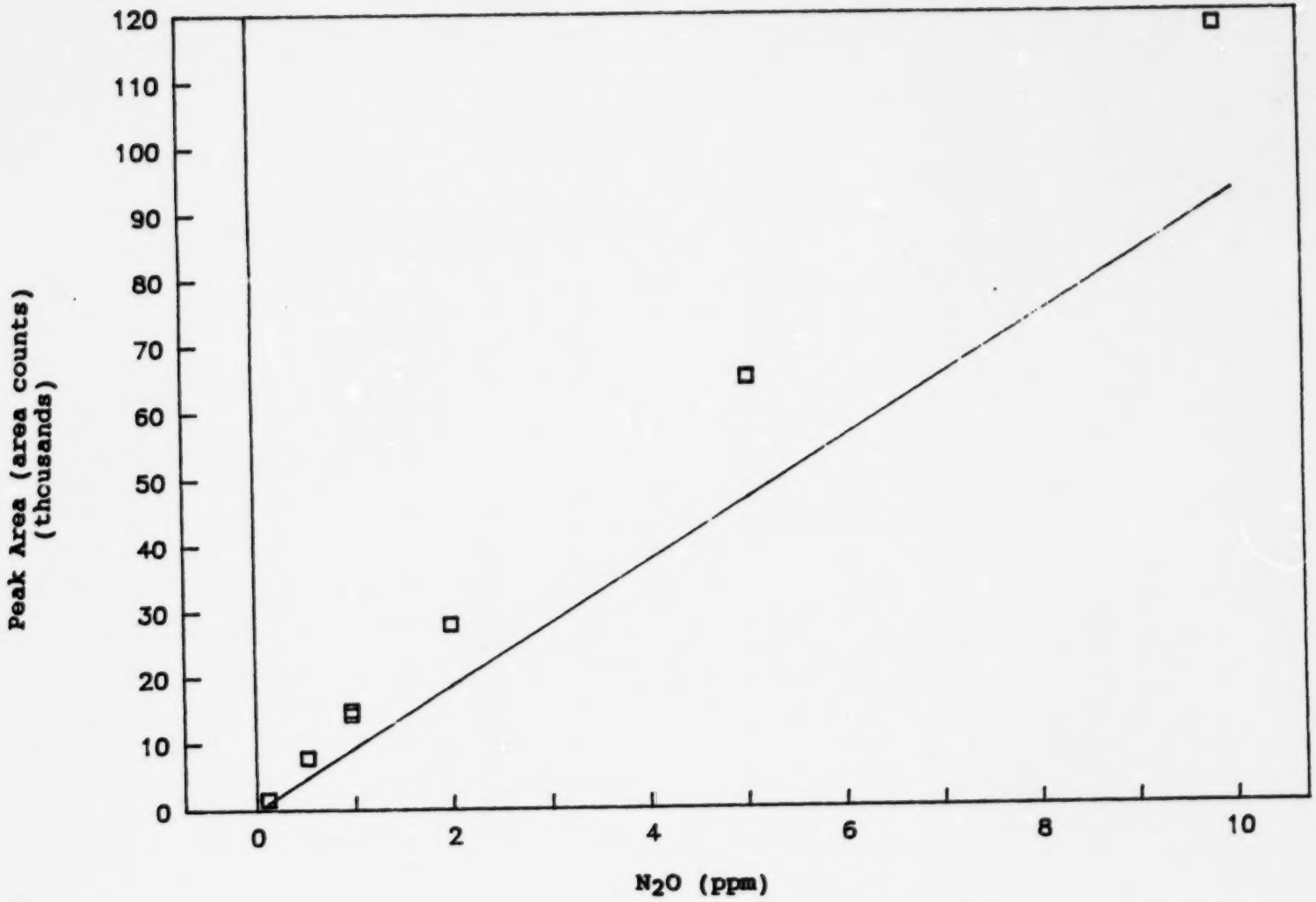


Figure 3. ECD response: expanded view of lower range.

$$\ln(x) = \frac{\ln\left[\frac{y}{a}\right]}{b} \quad (3)$$

$$x = \left(\frac{y}{a}\right)^{1/b} \quad (4)$$

C. Calculate the percent difference (D) between the true N_2O concentration and the concentration derived from the calibration curve through back-calculation, where:

$$D = [(N_2O_{curve} - N_2O_{true})/N_2O_{true}] \times 100 \quad (5)$$

D. If $|D| \leq 10\%$ for each standard, the calibration is acceptable. Repeat the calibration if $|D|$ is $>10\%$.

E. Verify the relationship between the calibration curve and the three QC standards by introducing the standards to the GC in same manner that the instrument was calibrated.

F. Obtain duplicate data points for each standard and calculate the average peak area.

G. Calculate the concentration of each QC standard by applying the average peak area to the equations given in step B.

H. Use equation 5 from step C to calculate the percent difference between the true concentration and the concentration derived from the calibration curve. The $|D|$ must be 10%.

I. Use the QC standards to verify the integrity of the calibration after 1 hour of analysis during an on-line routine and after every third sample when analyzing grab samples.

J. Verify the effects of the sample conditioning system by introducing the QC standards at the combustion source.

   1. Disconnect the sample line at the combustion source outlet from the inlet of the sample conditioning system.

   2. Connect the QC cylinder to the conditioning system. Push the sample through all components of the system as if it were a sample originating from the combustion source.

K. Repeat the calculation in steps F through H. If $|D|$ is $\leq 15\%$, the sample conditioning system has not compromised the N_2O concentration.

NOTE

If N_2O concentration is compromised by the sample conditioning system, the source of contamination must be eliminated. When the contamination problem cannot be resolved, the multipoint calibration must be conducted with all standards passing through the conditioning system.

4.3 METHOD PRECISION/ACCURACY

Data accuracy is primarily a function of instrument calibration. Obtain a measure of method accuracy from performance audits and quality control checks (section 6.1). If the analytical system is out of control (error exceeds ±15% of the true concentration) and problems cannot be resolved through corrective action, recalibrate the analyzer. Data taken between the previous calibration and the corrective calibration should be considered suspect.

Precision is a function of analyzer stability. Obtain estimates of precision from the analytical system response to daily span and QC checks, using equation 7 (section 6.1). The error due to analyzed drift should not exceed 15% of the true value of the QC standard for the selected range.

SECTION 5

DATA REDUCTION

5.1 CALCULATIONS

The response of the ECD is a non-linear function of concentration. To evaluate the best fit of the data, full-scale calibrations were conducted on two analyzers manufactured by Hewlett Packard (HP) and Shimadzu (S). Two types of carrier gas, P-5 and P-10, were used with each analyzer. A review of the data indicates that the precision of triplicate data points is an increasing function of concentration. Figure 4 shows that standard deviation is approximately proportional to concentration. This suggests that a log transformation may be appropriate in order to have variability constant over the range of interest.

The usual approach to calibration, a least-squares regression on the original scales (ppm and peak area), would be appropriate if the objective is to minimize error on an absolute basis and if variability were independent of concentration. In such a case, error could be reported as less than a certain concentration, which could also be reported as a percentage of full scale. A problem with this type of error control and estimate is that the estimated error for low concentrations will be very large relative to the measured or true concentration.

By performing a linear regression in terms of log units (i.e., transforming the data), the operator would be able to control and report error on a relative basis. Relative error improves as transformed data are applied to higher order regressions. Beyond the second order (quadratic), however, the improvement is not statistically significant.

During field studies, N_2O concentrations will be determined through a first-order regression. An example calculation using the HP/P-5 calibration follows Table 1. For final reporting, the results may be compared to a second-order regression.

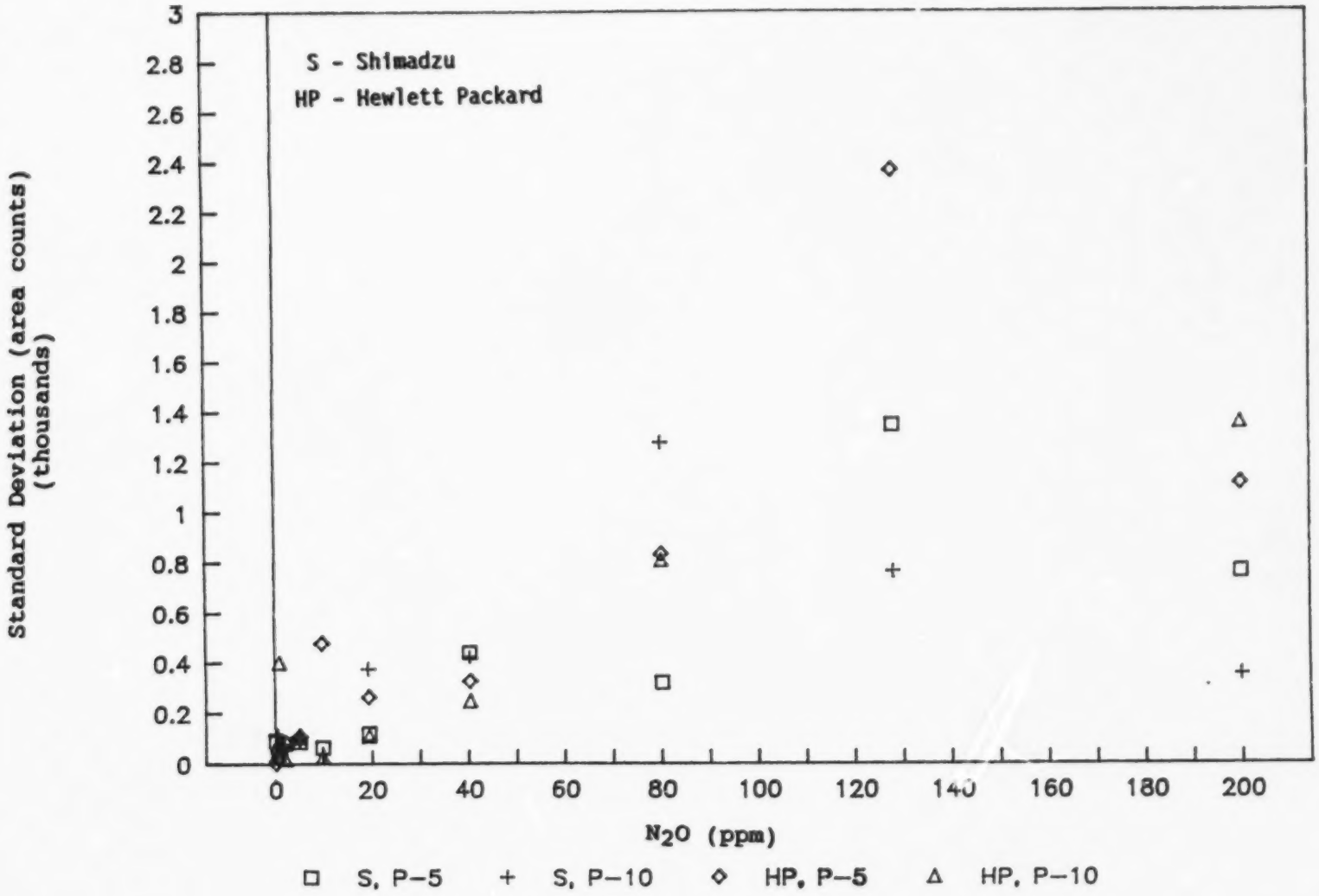


Figure 4. Standard deviation for calibrations with P-5 and P-10 carriers.

TABLE 1. RESULTS OF FIRST-ORDER LINEAR REGRESSION (LOG MODEL)

Instrument Carrier	ln(a)	b	Error (%)		
			1-5 ppm	5-40 ppm	40-200 ppm
HP/P-5	9.5328	0.8828	4.3	4.2	2.7
HP/P-10	9.6289	0.8747	3.7	4.2	2.6
S/P-5	9.2185	0.9195	4.1	4.7	3.0
S/P-10	9.2123	0.9222	4.4	4.7	3.0

Equation:

$$\ln(y) = \ln(a) + b[\ln(x)]$$

$$\ln(x) = \frac{\ln(y) - \ln(a)}{b}$$

$$x = \left(\frac{y}{a}\right)^{1/b}$$

Example Calculation

True concentration = 0.514 ppm
Average response = 7874 area units

$$x = \left(\frac{7874}{e^{9.5328}}\right)^{1/0.8828}$$

$$x = (0.5704)^{1.1328}$$

$$x = 0.529$$

$$\text{Error} = \frac{0.529 - 0.514}{0.514} \times 100$$

Error = 3.0%

The regression coefficients and the magnitudes of the relative error (average) from the HP and Shimadzu calibrations are given in Table 1. Figure 5 shows the fit of the first-order regression for the HP with a P-5 carrier gas. Table 2 shows the regression coefficients and average relative errors for a second-order regression.

5.2 DATA MANAGEMENT

A. Validation - Recheck all data prior to reporting. Validation must be conducted by the project or test leader.

B. Reporting - Report all data on standard forms signed by the test operator and data validator. Include estimates of accuracy (percent error) and precision (standard deviation) based on daily calibration and QC checks and the results of performance audits. Report the number of data points used to calculate the precision and accuracy. Also include an explanation of any missing or suspect data (i.e., outliers).

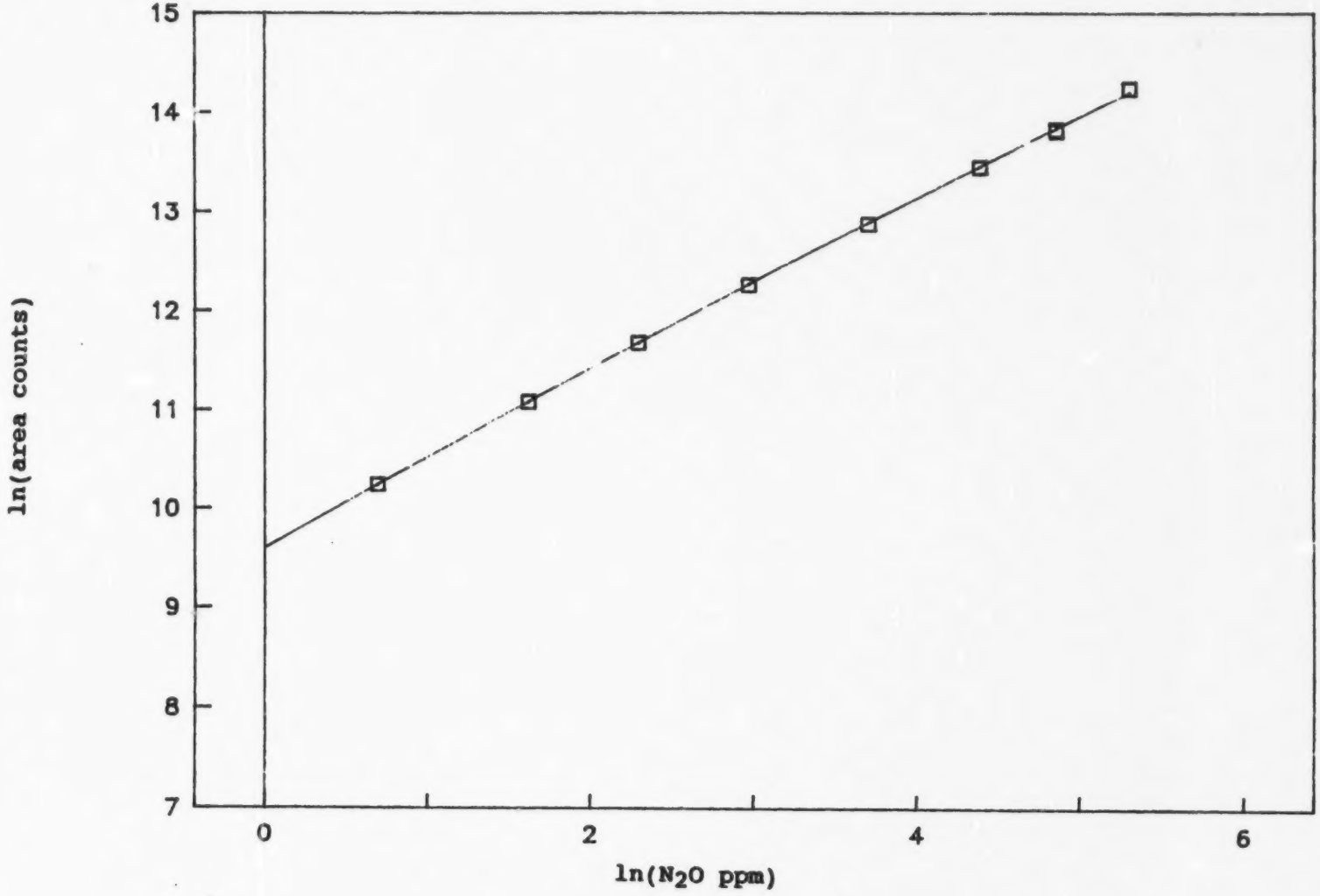


Figure 5. First-order regression: HP calibration with P-5 carrier.

TABLE 2. RESULTS OF SECOND-ORDER (QUADRATIC) LINEAR REGRESSION (LOG MODEL)

Instrument Carrier	ln(a)	b	c	Error (%) 1-5 ppm	5-40 ppm	40-200 ppm
HP/P-5	9.5144	0.9369	-0.0111	3.0	0.5	1.0
HP/P-10	9.6112	0.9264	-0.0110	1.2	0.6	2.0
S/P-5	9.1979	0.9801	-0.0129	1.7	0.8	1.7
S/P-10	9.1912	0.9842	-0.01318	2.0	0.6	1.7

Equation: $\ln(y) = \ln(a) + b[\ln(x)] + c\{[\ln(x)]^2\}$

SECTION 6

QUALITY ASSURANCE/QUALITY CONTROL

6.1 QC CHECKS

During a series of tests, analyze a QC sample from a cylinder containing a verified concentration that is approximately 50% of the full-scale of the working range. The QC check should be conducted every hour during on-line analysis and after every third sample (i.e., after nine measurements for triplicate analysis) during grab sample analysis. Calculate the cylinder concentration from the instrument response and the appropriate calibration curve. Compare the calculated value to the cylinder's true value and report the error as a percentage of the true value, according to:

$$N_2O_{error} = \frac{N_2O_{calc.} - N_2O_{true}}{N_2O_{true}} \times 100 \qquad (6)$$

Errors greater than ±15% are unacceptable and indicate the need for corrective action. Gas cylinders containing less than 689.25 kPa (100 psig) must not be used as calibration or QC standards.

The triplicate and duplicate data points generated by the calibration standards and QC samples should be used to calculate precision by:

$$s = \sqrt{\left[n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2 \right] / n(n-1)} \qquad (7)$$

where: n = number of data points
x_i = individual data points.

6.2 QC CONTROLS

A. Documentation

1. Laboratory Notebook - Keep all test results, calibration data, and quality control data in a bound laboratory notebook. Sign and date the notebook at the time of data entry.

2. Instrument Notebook - Assign a logbook to the GC. Use the logbook to maintain a record of all calibrations, maintenance, and repairs.

3. Certification/Verification - In a secure area, maintain a file of manufacturer's certifications and laboratory verification of standards.

4. Instrument Manuals - Keep operator's manuals for all components of the analytical system available and easily accessible.

B. Raw Data - Maintain all measurement data (storage diskettes, printouts) on file in a secure area.

C. Internal/External Audits - Audit the GC performance by challenging the system with verified concentrations of N_2O unknown to the system operator. If the system fails the audit with error greater than ±15%, it is out of control; take corrective action. Maintain a file of performance audit results and corrective actions.

SECTION 7

BIBLIOGRAPHY

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